

The scaling behaviour of screened polyelectrolytes

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(received ; accepted)

PACS. 05.20-y - .

PACS. 36.20-r - .

PACS. 64.60-i - .

Abstract. – We present a field-theoretic renormalization group (RG) analysis of a single flexible, screened polyelectrolyte chain (a Debye-Hückel chain) in a polar solvent. We point out that the Debye-Hückel chain may be mapped onto a *local* field theory which has the same fixed point as a generalised $n \rightarrow 1$ Potts model. Systematic analysis of the field theory shows that the system is one with two interplaying length-scales *requiring* the calculation of scaling functions *as well* as exponents to fully describe its physical behaviour. To illustrate this, we solve the RG equation and explicitly calculate the exponents and the mean end-to-end length of the chain.

Polyelectrolytes are polymers with ionizable monomers which in polar solvents, such as water, dissociate into charged polymers and small ‘counter-ions’ of opposite sign. They are of widespread importance with many applications in physics, biology and chemistry [1]. Their solubility in polar solvents means that they also have many industrial applications. Typical examples are DNA and sulphonated polystyrene.

The behaviour of polyelectrolytes is quite poorly understood, chiefly because it has been difficult to deal with their long-range coulomb interactions theoretically. In addition, counterions, complex-formation and salt and their differing length-scales make comparison between theory and experiment difficult because of questions of validity of the theories in different regimes. Neutral polymers on the other hand, have been extremely successfully described by scaling ideas and renormalization group theories [2]. The separation of the length-scales in their physics leads to *universality*. The main properties of the system are independent of microscopic details which only change prefactors in the physical quantities and make analysis of experimental results, at least in their limiting behaviour, reasonably straightforward. It would be particularly useful if the behaviour of polyelectrolytes could also be put in a similar context. The resulting theory would obviously be more complicated reflecting the increased complexity of the system. Nonetheless a ‘universal’ theory of polyelectrolytes would be a real

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step forward in the understanding of polymer solutions. This is what we attempt to do in this paper. In this spirit we consider the simplest possible system, a single charged chain in solution.

In solution the counter-ions in the vicinity of the macro-ion(polymer) ‘screen’ or reduce the range of the coulombic interaction. The simplest model of a screened polyelectrolyte which we use as the starting point for our analysis is the Wiener chain with a Debye-Hückel (DH) or Yukawa potential interaction between charged monomers. The chain is described by a vector $\mathbf{r}(s)$ parametrised by the arc-length s and the partition function is obtained from $Z = \int \mathcal{D}\mathbf{r}(s) \exp \{-\beta \mathcal{H}_{DH}[\mathbf{r}(s)]\}$ with the Hamiltonian of the system given in d dimensions by

$$\beta \mathcal{H}_{DH} = \frac{d}{2\ell} \int_0^L ds \left(\frac{\partial \mathbf{r}}{\partial s} \right)^2 + b \int_0^L \int_0^L ds ds' V(\mathbf{r}(s) - \mathbf{r}(s')), \quad (1)$$

where ℓ is the ‘Kuhn-segment’ length of the chain, $L = \ell N$ the length of the chain, where N is the number of segments on the chain. The Kuhn-length here refers to the distance between *charged* monomers (see inset Fig.1). $1/\beta = k_B T$ and $b \propto \lambda_B$ where $\lambda_B = \frac{q^2}{4\pi\epsilon\epsilon_0 k_B T}$ is the Bjerrum length which measures the strength of the bare coulomb interaction. In water, $\lambda_B = 7.14 \text{ \AA}$. As usual $\epsilon\epsilon_0$ is the dielectric constant of the solvent, k_B is the Boltzmann constant and T the temperature. The potential between monomers, $V(\mathbf{r})$ is a solution of the linearised Poisson-Boltzmann equation $(-\Delta + \kappa^2)V(\mathbf{r}) = 0$ which in three dimensions is given by the usual $V(\mathbf{r}) = e^{-\kappa|\mathbf{r}|}/|\mathbf{r}|$. The screening length or range of the interaction is given by $1/\kappa$ and $\kappa \propto \sqrt{\lambda_B}$ is a function of the density of screening ions and the dielectric properties of the solution. The DH model [3] is thought to be valid only when the polyelectrolyte is weakly charged (see inset Fig.1) and in the presence of salt. There are no large fluctuations in the counter-ion/salt density so for the Coulomb interaction the DH model may be considered to be ‘mean-field’.

Recent extensive simulations of flexible DH chains [4] give dramatically different results from existing theories [5, 6]. We compare our results with these simulations because experiments are always performed at non-zero concentrations where many-chain effects begin to play a part and cannot be used to check the validity of a single chain model [1]. The quantity that we want to calculate is the average end-to-end length $\langle R^2 \rangle \equiv \langle (r(L) - r(0))^2 \rangle$.

Returning to equation (1), we apply a generalisation of the well known de Gennes trick to map the polyelectrolyte to an $n \rightarrow 0$ field theory [7] with a non-local (long-ranged) interaction [8, 9]. The propagator is defined in the usual way as the Laplace transform (LT) of the 2-point function $G(\mathbf{R}) \equiv \int [\mathcal{D}\phi] \phi(\mathbf{R}) \phi(\mathbf{0}) e^{-S(\phi)} = \int_0^\infty d\mathcal{L} e^{-t\mathcal{L}} \langle \delta(\mathbf{r}(\mathcal{L}) - \mathbf{r}(0) - \mathbf{R}) \rangle$ where $\mathcal{L} = 2L\ell/d = 2N\ell^2/d$ with the action given by $S(\phi) = \int_{\mathbf{r}} \left[\frac{1}{2}(\nabla\phi)^2 + \frac{1}{2}t\phi^2 \right] + \frac{g}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \phi^2(\mathbf{r}) V(\mathbf{r} - \mathbf{r}') \phi^2(\mathbf{r}')$ where $2g = (2\ell/d)^2 b$ and $\phi(\mathbf{r})$ are $n \rightarrow 0$ component fields with $O(n)$ symmetry. We have used the notation $\int_{\mathbf{r}} \equiv \int d^d r$. We perform a Hubbard-Stratonovich transformation [8] to remove the DH potential and generate a new scalar field $\psi(\mathbf{r})$ so that

$$G(\mathbf{R}) = \int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q}\cdot\mathbf{R}} \tilde{G}(q) = \mathcal{N} \int [\mathcal{D}\phi] [\mathcal{D}\psi] \phi(\mathbf{R}) \phi(\mathbf{0}) e^{-S(\phi, \psi)} \quad (2)$$

$$\text{with } S(\phi, \psi) = \int_{\mathbf{r}} \left[\frac{1}{2}(\nabla\phi)^2 + \frac{1}{2}t_2^{(0)}\phi^2 + \frac{1}{2}(\nabla\psi)^2 + \frac{1}{2}t_1^{(0)}\psi^2 + \frac{1}{3!}u_0\phi^2\psi \right] \quad (3)$$

where $t_2^{(0)}$ is the polyelectrolyte fugacity, $t_1^{(0)} = \kappa^2$ and \mathcal{N} is a normalisation factor. The coupling is given by $u_0/3! = i\sqrt{g}(\sqrt{g})$ if ψ is real(imaginary). $\psi(\mathbf{r})$ is a fluctuating Coulomb field which is coupled to the polymer density. It has fluctuations on a length-scale given by $1/\kappa$. Since there are two independent fields, we have two sets of exponents $\nu_\psi, \nu_\phi; \eta_\psi, \eta_\phi$. To distinguish between the two we use a superscript ψ for the Coulomb terms and a superscript

ϕ for the polymer terms.

There is a rich literature on the use of the RG and field theory to calculate the properties of neutral polymers. On the other hand, these techniques have not been applied successfully to charged polymers, polyelectrolytes. This was due to a misconception that they could not be usefully applied to such systems in the physical dimension, $d = 3$. In the literature on field theory and renormalization group theory of polyelectrolytes [8, 9, 10], work has always been done on unscreened chains. This has led to an unfortunate obscuring of the physics which we believe we have finally clarified. The exponents ν_ϕ can be calculated to all orders in $\epsilon = 6 - d$ (the upper critical dimension $d_c = 6$ can be inferred from the Lagrangian (3)) and is given by $\nu_\phi = 2/(d - 2)$ [9]. It has always been assumed that the end-to-end length is given by

$$\langle R^2 \rangle \sim \ell^2 N^{2\nu_\phi} \quad (4)$$

and since $\nu_\phi = 1$ in $d = 4$, and the chain could not be stretched out more than a rod, $\langle R^2 \rangle \not\propto \ell^2 N^2$, it was said that due to overstretching of the Gaussian chain the theory breaks down for $d < 4$. It was therefore thought that field theoretic methods could not be used on charged chains in the physical dimension $d = 3$. We will show that this analysis is incomplete.

We have a number of new results in our letter. Firstly, we point out a connection between a Potts model used to study percolation and the sol-gel transition and a single polyelectrolyte chain [11]. Secondly, we include the two *important* length-scales which are necessary for the analysis of the system. They are the screening-length $1/\kappa$ and the gaussian chain size $S = \langle R_0^2 \rangle^{1/2} = \ell N^{1/2}$. A wide range of systems can be studied beginning where the screening is very high (SAW), $\kappa^2 \ell^2 N \gg 1$ (the polymer field ϕ is more critical than coulomb field ψ) and ending where it is very low (unscreened, rod-like), $\kappa^2 \ell^2 N \ll 1$ (ψ is more critical than ϕ). This is therefore a problem of cross-over [12]. The previous work has focussed, in our opinion mistakenly, on the unscreened case by setting $\kappa = 0$. The exponent ν_ϕ is actually calculated for the intermediate regime $\kappa^2 \sim 1/(\ell^2 N) \rightarrow 0$ and *does not* apply to the unscreened (rod) regime where $\kappa \rightarrow 0$ **and** $\kappa^2 \ell^2 N \rightarrow 0$. We also find that quantities like the end-to-end distance depend on negative powers of κ . This implies that the operator $\int_r \kappa^2 \psi^2$ in eqn. (3) is dangerously irrelevant [14]. By setting $\kappa = 0$ at the start of the calculation, one loses sight of such subtleties.

We calculate in agreement with earlier work [8, 9] the exponents

$$\eta_\phi = -\frac{\epsilon}{4} - \frac{9\epsilon^2}{32} + O(\epsilon^3), \quad \eta_\psi = 0, \quad \nu_\psi = \frac{1}{2}, \quad \nu_\phi = \frac{2}{d-2} + O(\epsilon^3); \quad (5)$$

where $\epsilon = 6 - d$. The exponents can also be obtained from the percolation theory but at a different fixed point from the usual sol-gel transition [11]. This leads naturally to our final conclusion: these exponents correspond to a **bi-critical** fixed point (both ϕ, ψ are critical) where the screening length and the chain size are comparable and at this fixed point the end-to-end length we calculate as

$$\langle R^2 \rangle \sim \ell^2 N^{2\nu_\phi} f(\bar{\kappa}^{1/\nu_\phi} N) \quad (6)$$

where $\bar{\kappa}/\ell = \kappa$ and $f(x)$ is a function *singular* as $x \rightarrow 0$. We *explicitly* calculate $f(x) = x^{(-2\nu_\phi+1)} g(x)$ where $g(x) = (1 - 3\epsilon \log(x)/(4x)) [1 - \epsilon(3\gamma/(4x) - 5/24)] [1 - \epsilon(3/(4x) - 1/2 + x/8) \exp(x) E_1(x)] + O(\epsilon^2)$. The exponential integral $E_1(z)$ is defined by $E_1(z) = \int_1^\infty dt \exp(-zt)/t$ and $\gamma = 0.57721$ is Euler's constant. The end-to-end length is given by

$$\langle R^2 \rangle \sim \ell^2 \frac{N}{\bar{\kappa}^2} \bar{\kappa}^{1/(\nu_\phi)} g(\bar{\kappa}^{1/\nu_\phi} N) \sim \ell^2 N^{2-1/(2\nu_\phi)} g(\bar{\kappa}^{1/\nu_\phi} N) \quad (7)$$

(Recall that at this fixed point $\kappa^2 \sim 1/(\ell^2 N) \rightarrow 0$). Earlier work [8, 9] had always *implicitly* assumed that $f(x)$ was a well behaved function in the limit $x \rightarrow 0$ ($\kappa \rightarrow 0$). We find

$2\nu'_1 = 2 - 1/(2\nu_\phi)$ determines the chain size and *not* $2\nu_\phi$. Also, because of g the exponent will vary slightly with κ [4]. There is consequently no over-stretching (at this fixed-point, $u_*^2 = -27\epsilon/4$) for $d < 4$ and equation (4) should be replaced by equation (7). It is important to note that $\nu'_1 = 7/8 = 0.875$ (intermediate between the SAW, $\nu = 0.588$ and rod, $\nu = 1.0$) in three dimensions. It is also clear from our analysis that the lower critical dimension is $d = 2$ where the theory breaks down.

In order to compare with earlier approaches we may ‘fit’ our results from equation (7) to a worm-like chain model [13]. The electrostatic persistence length, $\bar{\ell}_e$, may be estimated from $\bar{\ell}_e(1 - e^{-N\ell/\bar{\ell}_e}) \propto \bar{\kappa}^{\nu'_2} g(\bar{\kappa}^2 N^4)$ with $\nu'_2 \simeq -3/2$ in $d = 3$ showing no unique power law behaviour. This is in agreement with the simulations of Micka and Kremer [4]. The rod-like behaviour in the long-range, low salt regime $1/\kappa^2 \gg \ell^2 N$ and the self-avoiding walk behaviour for the short-range, high salt regime, $\ell^2 N \gg 1/\kappa^2$ [17] can be obtained using different methods [1].

Now we perform a RG analysis of our model with Lagrangian given by equation (3). Our goal is to calculate

$$\langle R^2 \rangle = -\mathcal{T}_\mathcal{L}^{-1}(\partial_{q^2} \tilde{G}(q)|_{q=0})/\mathcal{T}_\mathcal{L}^{-1}(\tilde{G}(q)|_{q=0}) = D(u)F(\mathcal{L}, t_1) \quad (8)$$

where $D(u)$ is a non universal constant, $\mathcal{T}_\mathcal{L}^{-1}$ is the inverse LT with respect to \mathcal{L} and $\tilde{G}(q) \equiv \tilde{G}^{(2,0)}(q)$ is the FT of the renormalised chain propagator. The bare parameters are expressed in terms of their renormalized values by $u_0 = \mu^{\epsilon/2} S_d^{-1} Z_u u$, $t_1^{(0)} = \mu^2 Z_\psi^{-1} [t_2 Z_{\psi, \phi^2} + t_1 Z_{\psi, \psi^2}]$ and $t_2^{(0)} = \mu^2 Z_\phi^{-1} [t_2 Z_{\phi, \phi^2} + t_1 Z_{\phi, \psi^2}]$ where μ^{-1} is an external length-scale and $S_d = \Omega_d/(2\pi)^d$ with Ω_d the angular part of a d -dimensional integral. We denote an N point polymer M point coulomb vertex function as $\Gamma^{(N,M)}$ while a composite N point polymer M point coulomb vertex function with L , ϕ^2 and K , ψ^2 insertions is generally given by $\Gamma^{(N,L;M,K)}$. The wave-function renormalization factors are calculated by expressing the renormalized vertex functions in terms of the bare ones as $\Gamma_R^{(N,M)} = Z_\phi^{N/2} Z_\psi^{M/2} \Gamma^{(N,M)}$. The Z -factors are evaluated using the vertex functions which are calculated using a dimensional regularisation scheme with minimal subtraction of poles [14]. We begin with the Coulomb vertex $\Gamma^{(0,2)}$ which due to the $n \rightarrow 0$ limit gives the result $Z_\psi = 1$ because all closed subdiagrams composed of these polymer lines give a factor n . From the polymer vertex $\Gamma^{(2,0)}$ we get Z_ϕ . For the determination of Z_u we need the leading singular $1/\epsilon$ contribution of $\Gamma^{(2,1)}$ from which follows the β -function the zero of which yields the infra-red stable fixed point $u_*^2 = -27\epsilon/4$. An evaluation of $\Gamma^{(0,0;2,1)}$ yields $Z_{\psi, \psi^2} = 1$ and $\Gamma^{(0,1;2,0)}$ gives $Z_{\psi, \phi^2} = 0$ using similar arguments as those for Z_ψ . The composite polymer vertex function $\Gamma^{(2,1;0,0)}$ gives Z_{ϕ, ϕ^2} and $\Gamma^{(2,0;0,1)}$ to 1-loop yields $Z_{\phi, \psi^2} = Z_{\phi, \phi^2} - 1$.

To see the scaling form of $\langle R^2 \rangle$, we need to solve the RG equation for $\mathcal{G}(q) \equiv \mathcal{T}_\mathcal{L}^{-1}[\tilde{G}_R^{(2,0)}(q)]$ which is given by

$$(\mu\partial_\mu + \beta_u\partial_u - 2t_1\partial_{t_1} - \vartheta_2\mathcal{L}\partial_\mathcal{L} + \gamma_\phi - \vartheta_2 - \vartheta_1 t_1 \mathcal{L}) \mathcal{G}(q/\mu; u, \mathcal{L}, t_1) = 0. \quad (9)$$

where $\beta_u = (\partial u / \partial \ln \mu)$, $\gamma_\psi = \beta_u \partial_u \ln Z_\psi$, $\gamma_\phi = \beta_u \partial_u \ln Z_\phi$, $\gamma_{\phi^2} = \beta_u \partial_u \ln Z_{\phi, \phi^2}$, $\vartheta_1 = -Z_\phi / Z_{\phi, \phi^2} \beta_u \partial_u [Z_{\phi, \psi^2} / Z_\phi]$ and $\vartheta_2 = -2 - \gamma_{\phi^2} + \gamma_\phi$ and we have used the notation $\partial_x A = \partial A / \partial x$. The solution is readily obtained using the method of characteristics [14] giving

$$F(\mathcal{L}, t_1) = \mathcal{L}^{2\nu_\phi} F_1(1, t_1 \mathcal{L}^{2\nu_\phi}, u_*) = 1/t_1 F_2(\mathcal{L} t_1^{1/(2\nu_\phi)}, 1, u_*) \quad (10)$$

showing non-trivial scaling ($\eta_\phi = \gamma_\phi(u_*), \nu_\phi^{-1} - 2 = \gamma_{\phi^2}(u_*) - \gamma_\phi(u_*)$). This means that the scaling function must be explicitly calculated to extract information about the size of the chain. Great care must be taken in the interpretation of the inverse Laplace transform. As we are dealing with critical fields, the masses t_1 and t_2 must go to zero. We get non-trivial results

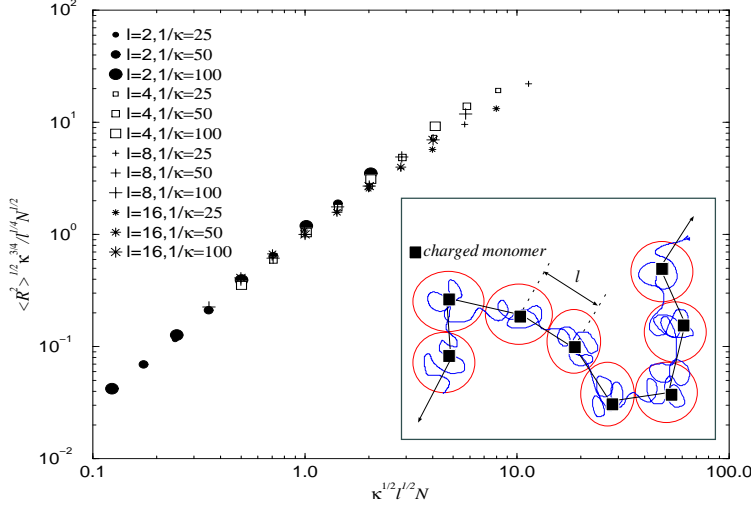


Fig. 1. – We plot Micka and Kremer’s [4] 3d simulation data of flexible DH chains for different values of ℓ , N and κ . $\sqrt{\langle R^2 \rangle \kappa^{2-1/\nu_\phi} / N}$ vs $\kappa^{1/\nu_\phi} N$ with $\nu_\phi = 2/(d-2)$ evaluated at $d = 3$ and we get *all* the points to collapse on one curve. Inset: weakly charged polyelectrolyte and Kuhn length ℓ .

only when *both* length-scales are large and of the same order otherwise the larger length-scale dominates the physics and the smaller becomes irrelevant. This means that the ratio of the two length-scales $c = \frac{\ell}{1/\kappa^2}$ must be finite. This gives the non-trivial fixed-point $u^* \neq 0$. It is reassuring to note that the explicit calculation, (7), agrees *exactly* with the general form of the scaling function in equation (10).

As is usual in RG analysis one must check for stability of the fixed point as the quartic terms become relevant as we cross the dimension $d = 4$. This says something about the validity of the DH model (which assumes these operators are irrelevant) in the physical dimension $d = 3$. Any operators which make the fixed-point unstable are **corrections** to DH theory. The ψ^4 and $\psi^2\phi^2$ and $(\phi^2)^2$ are allowed by symmetry and become relevant for $d < 4$ [9]. The excluded volume term $(\phi^2)^2$ is only relevant in the high salt regime. The quartic corrections mean that the DH model is invalid below $d = 4$ in the limit $\kappa \rightarrow 0$ because the critical fluctuations of the Coulomb field for $d < 4$ mean that it cannot be described by a Gaussian model (no terms higher than quadratic in ψ) [15]. Since we know that DH theory is in a sense a ‘mean-field’ approximation, we should expect it to be wrong in low dimensions. Therefore ν_ϕ is valid for the DH model for $d < 4$ but not for the *complete* theory (DH + corrections). The approximation that the fluctuations in the density of the screening ions are small breaks down. This does not really have anything to do with $\nu_\phi > 1, d < 4$ which is a **result** of a field theory of a DH chain.

Flexible polyelectrolytes have been simulated by Stevens and Kremer [16] using explicit counter-ions and Micka and Kremer [4] using a DH potential. Stevens and Kremer [16] found exponents $\nu_1 \simeq 0.94 < 1$ in good agreement with our picture. Micka and Kremer [4] observed no unique power law as κ and L were varied. In Fig.1 we plot their end-to-end data using our explicit scaling form in equation(7) and get very good agreement. More detailed comparison

of this and other quantities with their numerical data will be presented elsewhere [17].

In conclusion, we have systematically calculated the properties of a single screened polyelectrolyte in the Debye-Hückel approximation (a well-defined problem) and found non-trivial scaling behaviour in good agreement with simulation. The DH model is therefore controlled by *three* fixed points governed by $c = \ell^2 N \kappa^2$. They are $c \rightarrow \infty$ (SAW), $c \simeq 1$ the new non-trivial behaviour which is the subject of this paper and $c \rightarrow 0$ (rod). Our analysis confirms that the DH model breaks down if there are large fluctuations in the coulomb field, as would be observed in counter-ion condensation. We hope that this paper will stimulate the interest in a 20 year old problem in the literature, our conclusion being that the calculation of the exponents by Pfeuty et al and others [8, 9, 10] was absolutely correct but their interpretation of those exponents and hence of the physics was incomplete. We believe that this paper therefore re-opens the area of the field theoretic RG description of charged polymers. In future publications we will deal with charged manifolds, directed polyelectrolytes, solutions and networks [17].

We acknowledge helpful discussions with M.E. Cates, S.F. Edwards, H-K. Janssen, J-F. Joanny, M. Kardar, K. Kremer, A. Liu, U. Micka, K. Müller-Nedebock, J. Rudnick, M. Schmidt, B. Söderberg, D. Thirumalai, T. Vilgis and T. Witten. We thank L. Schäfer for pointing out reference [9]. We particularly thank K. Kremer and T. Vilgis for a critical reading of the manuscript.

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